



ELSEVIER

Journal of Electron Spectroscopy and Related Phenomena 114–116 (2001) 501–506

JOURNAL OF
ELECTRON SPECTROSCOPY
and Related Phenomena

www.elsevier.nl/locate/elspec

Multilayer relaxation of the Al(100) and Al(110) surfaces: an ab initio pseudopotential study

Jin-Cheng Zheng, Hui-Qiong Wang, C.H.A. Huan*, A.T.S. Wee

Department of Physics, National University of Singapore, Lower Kent Ridge Road, Singapore 119260, Singapore

Received 8 August 2000; received in revised form 28 September 2000; accepted 3 October 2000

Abstract

The multilayer relaxations of Al(100) and Al(110) surface are studied using the plane wave ab initio pseudopotential method within the local density functional theory. Our calculations show that the surface relaxation of Al(100) is an ‘anomalous’ outward relaxation, which is in excellent agreement with experimental results, although several previous empirical and semi-empirical theoretical studies have predicted contractions that are contrary to the experiments. For the Al(110) surface, our calculations do show inward relaxation, which is consistent with LEED experiments and other theoretical calculations. The origin of ‘inward’ and ‘outward’ relaxation is discussed. The surface energy is also studied in this work. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ab initio pseudopotential; Surface relaxation; Al(100) surface; Al(110) surface; Surface energy

1. Introduction

Knowledge of the geometrical arrangement of the atoms near the surface is a basic ingredient for the study of structural and dynamic properties of a metal surface. Recent studies of the structure of open metal surfaces have revealed the existence of relaxation phenomena extending several layers into the solid [1]. The study of this phenomenon has proved to be a useful testing ground for the refinement of experimental methods of structure determination and for the development of quantitative theories of surface electronic and geometrical structure [2].

Many theoretical calculations and experimental

measurements have been performed on surface relaxation of fcc metals [1–18]. In experimental measurements, low energy electron diffraction (LEED) is the main tool for investigating surface relaxation [4,11–14], while in theoretical calculations, empirical and semi-empirical methods [1,6,7,9,16,17] as well as first principle calculations [3,5,15,19] have been performed to determine the surface structure and surface energy. However, some drawbacks in semi-empirical methods such as effective-crystal theory (ECT) [7], effective medium theory [9] and embedded atom methods (EAM) [6] have been found in calculating surface relaxation and stress. For example, the surface stress values obtained using the semi-empirical potentials are usually significantly smaller than those obtained by first-principle calculations. These semi-empirical methods tend to predict inward relaxation of fcc metal surfaces, even for the

*Corresponding author. Tel.: +65-874-26-13; fax: +65-777-61-26.

E-mail address: phyhuana@nus.edu.sg (C.H.A. Huan).

‘anomalous’ surfaces of Al(100) [4], Al(111) [6,7,20,21], Pt(111) [22,23] and Cu(111) [24], which clearly show outward relaxation from experimental measurements. Therefore, the calculated surface stress for these relaxed surfaces are not sufficiently reliable by conventional semi-empirical methods. It has been suggested that the normal semi-empirical methods lack the microscopic detail in the description of the electronic structure [1]. Therefore, careful calculations from first-principle methods are still needed to understand both the normal inward and ‘anomalous’ outward surface relaxations.

In this work, we have used plane wave ab initio pseudopotential method within the local density functional (LDF) theory to calculate the multilayer relaxation of the Al(100) and Al(110) surfaces.

2. Method of calculation

Our calculations are performed with the plane wave ab initio pseudopotential method within the local density functional (LDF) theory. The Hedin-Lundqvist [25] form of the exchange-correlation potential and a mixed basis representation are employed. Non-local norm-conserving pseudopotentials are created according to the prescription of Hamann et al. [26]. The wave functions are expanded into plane waves up to a cutoff energy of 12.5 Ry. The k integration over the Brillouin zone is performed on

an $8 \times 8 \times 1$ Monkhorst-Pack mesh. Our total energy calculations are based on slab geometry in which multiple surfaces are presented. The top view of the Al(100) and Al(110) surfaces are showed in Fig. 1. The supercell contains nine (or 11) layers of Al and a vacuum layer of thickness ~ 8.5 Å. The slab is fully relaxed by the Hellman–Feynmann (H–F) force method and the criterion is for the H–F force to be less than 0.5×10^{-3} Ry au $^{-1}$.

3. Results

3.1. Surface relaxation

Firstly, we have performed calculations on bulk fcc Al metal. The equilibrium lattice constant is determined to be 7.46 au (about 3.95 Å), which is consistent with a recent first principle pseudopotential result [3] of 3.96 Å at cutoff energy of 11 Ry, and an experimental result of 4.02 Å at 0 K [27]. Then slab calculations are performed for the Al(100) and Al(110) surfaces.

The results of the surface multilayer relaxation for these surfaces are listed in Tables 1 and 2, respectively, together with experimental data and results by other theoretical methods. In both tables, Δd_{nm} is the percentage change in the interlayer spacing between layer n and layer m as compared to the bulk (ideal)

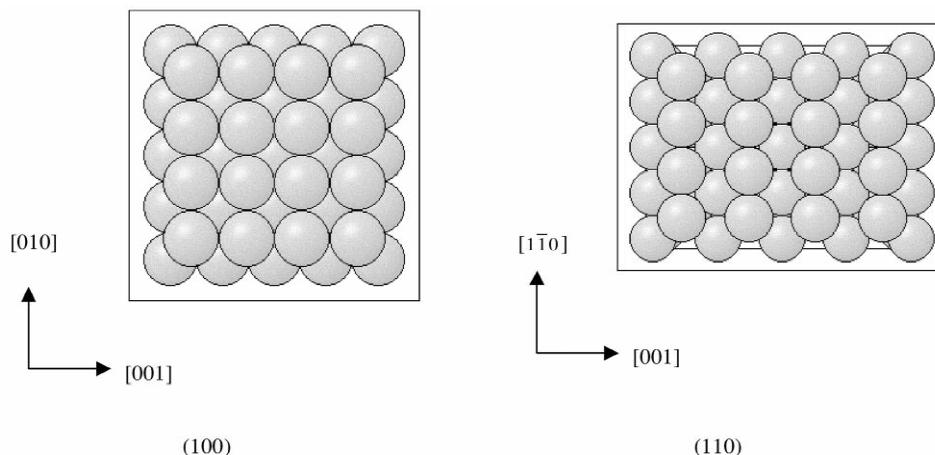


Fig. 1. Top view of the (100) and (110) surfaces of Al.

Table 1
Comparison of experimental and theoretical surface structure of Al(100)

Theory or experiment	Relaxation (%)				Method	Reference number
	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}		
Present study (nine layers)	1.89	4.12	2.96	2.94	Ab initio pseudopotential	
Experiment	1.8					[4]
Theory	0.79	0.06	0.01	0.00	MEAM	[1]
	1.2	0.2	-0.1		FP	[5]
	-4.9	-2.24	-2.25	-2.39	EAM	[6]
	-4.8	2.3			ECT	[7]
	<0				SEGF	[8]
	-1±2				SEGF	[10]
	-3			Effective-medium theory	[9]	

interlayer spacing. We will first discuss Al(100) surface, followed by the Al(110) surface.

It is well known that the surface relaxation behavior at an fcc metal surface is multifarious and complex. Although most surfaces of fcc metals show inward relaxation, there are a few surfaces that show ‘anomalous’ outward relaxation, Al(100) surface being a typical example along with several others such as Al(111), Pt(111) and Cu(111). There have been several previous studies on relaxation of the Al(100) surface by experiment [4] as well as with different levels of sophistication in the theoretical

calculations [1,5–9]. The experimental result shows an 1.8% outward relaxation for the Al(100) surface as reported by Davis et al. [4], while several semi-empirical theoretical calculations yielded inward relaxations. For example, a -3% inward relaxation is predicted by the effective-medium theory [9], -4.8% by ECT [7] and -4.9% by EAM [6]. Moreover, the surface-embedded Green’s function (SEGF) theory too gave inward relaxations [8,10]. All these results are clearly in conflict with the experimental data. In contrast, our calculations show an outward surface relaxation of +1.89% which

Table 2
Comparison of experimental and theoretical surface structure of Al(110)

Theory or experiment	Relaxation (%)				Method	Reference number
	Δd_{12}	Δd_{23}	Δd_{34}	Δd_{45}		
Present study (11 layers)	-7.68	5.15	-0.85	3.21	Ab initio pseudopotential	
Experiment	-8.5±1.0	5.5±1.1	2.2±1.3		LEED	[11]
	-8.6±0.8	5.0±1.1	-1.6±1.2	1.0±1.3	LEED (100 K)	[12]
	-8.4	4.9	-1.6		LEED	[13]
	-6.9	4.1	-3.7	1.7	LEED (70 K)	[14]
Theory	-6.1	5.5	-2.2	1.7	FP (8 layers)	[3]
	-7.4	3.8	-2.5	2.0	FP (15 layers)	[3]
	-9.64	2.71	4.30	-2.76	MEAM	[1]
	-10.47	3.64	-2.93	-1.45	EAM	[16]
	-9.1	1.3			ECT	[17]
	-11				SEGF	[10]
	-10.4	3.14	-2.75	1.4	FP	[19]
	-6.8	3.5	-2.4	1.6	FP	[15]
	-10	4	-3		Self-consistent	[18]

compares well with that from another previous first principle (FP) method of 1.2% by Bohnen and Ho [5], and in qualitative agreement with the modified embedded atom method (MEAM) of 0.79%. To check whether the outward relaxation is program (code) dependent, we use another ab initio pseudo-potential code [28] to calculate the multilayer relaxation of Al(100) and Al(110) surface. We get +1.98% for outward relaxation of Al(100) surface, which confirms our above results and indicates that the outward relaxation is program-independent. Our results also show that there is large expansion of the second layer (beneath the topmost layer) and that the expansion of the layers decreases with depth. This phenomenon is due to the effect of multilayer relaxation. We note that in the surface-embedded Green's function (SEGF) calculation [8], only the outermost layer has been allowed to relax while the subsurface interlayer spacings have been fixed, leading to the negative relaxation of the Al(100) surface. Thus inclusion of the effect of multilayer relaxations would probably resolve the contradictions between results obtained by SEGF with experimental data and those of FP calculations. However, it is very difficult to explain the origin of inward relaxation for the other non-FP methods.

For the Al(110) surface, most of the experimental data from LEED [11–14] show the same trends as can be seen from Table 2. The inward relaxation of Al(110) surface Δd_{12} range from -6.9 to -8.6% , and the expansion of the second layer Δd_{23} range is

between 4.1 and 5.5%. For Δd_{34} , some LEED experiments show contraction such as -3.7% [14] and -1.6% [12,13], while another available LEED experiment shows an expansion of 2.2% [11]. The only available experiments both show expansion of the 4th layer, i.e. $\Delta d_{45}=1.7\%$ [14] and $1.0\pm 1.3\%$ [12]. Previous theoretical studies show the usual behavior found for most metals, i.e. inward relaxation of the topmost layer, and our calculations also yield the result. The value of $\Delta d_{12}=-5.08\%$ (for the nine-layer slab) in this work is slightly smaller than experimental data and the other calculations. But there is significant improvement by increasing the slab to 11 layers, giving $\Delta d_{12}=-7.68\%$, $\Delta d_{23}=5.15\%$, $\Delta d_{34}=-0.85\%$ and $\Delta d_{45}=3.21\%$. Using another code [28], we get the $\Delta d_{12}=-8.95\%$, $\Delta d_{23}=2.46\%$, $\Delta d_{34}=-0.90\%$ and $\Delta d_{45}=2.18\%$. This trend of relaxation (oscillatory relaxations) as a function of layers (from surface to bulk) is generally found in experimental observations [12–14] and other FP calculations [3].

3.2. Surface energy

Table 3 compares our surface energy ($\text{eV } \text{\AA}^{-2}$) calculations with results from other methods as well as experiments for the Al(100) and Al(110) surfaces in relaxed and unrelaxed states. It can be seen that the surface energy decreases for both Al(100) and Al(110) due to relaxation. The change is 0.0041 eV

Table 3
Surface energy for Al(100) and Al(110) surface

Methods	Surface energy ($\text{eV } \text{\AA}^{-2}$)			
	(100) surface		(110) surface	
	Unrelaxed	Relaxed	Unrelaxed	Relaxed
This work	0.0713	0.0672	0.0748	0.0740
Other methods (MEAM [1])	0.0563	0.0562	0.0608	0.0591
Other methods (FP [15])				0.070 ± 0.002^a
EXP (polycrystalline)		0.0712 [34] 0.0737 [34] 0.0749 [35]		

^a The original data is 0.77 ± 0.02 (eV/surface atom).

\AA^{-2} for Al(100) while for Al(110) it is $0.0008 \text{ eV \AA}^{-2}$. The values obtained from our calculations for the relaxed surfaces agree rather well with experimental measurements. However, the comparison cannot be made directly since the experimental results are obtained from polycrystalline materials. It appears that our ab initio pseudopotential calculations yield results that are slightly larger than those by the semi-empirical MEAM [1], while being consistent with previous FP results [15]. One also finds that the surface energy of the Al(110) surface is larger than that of the Al(100) surface, as suggested by our current study (difference of $0.0068 \text{ eV \AA}^{-2}$) and from MEAM ($0.0029 \text{ eV \AA}^{-2}$) [1].

4. Discussion

There are several ways to explain why the topmost layer shows inward relaxation [1,29]: (i) when one cuts a crystal to form a surface, the electronic charge density relaxes so as to weaken its corrugation. The smoothing of the electron charge density reduces kinetic energy and results in the shift of electrons toward the surface. This attracts the positive ion cores closer to the rest of the crystal. (ii) Based on effective-medium theory (EMT) of metallic bonding [30–33], when a crystal is truncated to form a surface, the surface atoms which have lost electron density tend to move in such a way as to return to the optimal electron density and thus move toward the rest of crystal. (iii) The third explanation for topmost-layer contraction is that it is a natural consequence of the bond-order-bond-length correlation. Here the operative principle is saturation of valence. Every atom has a fixed number of valence electrons. If a surface is formed, the surface atoms lose several neighbors. The electrons that are involved in bonding to these neighbors therefore redistribute themselves nearer (i.e. ‘back-bonding’) to the atoms in the layer below. This strengthens the bond between the first and second atomic layers, thus it leads to an inward relaxation.

In this work, we find the Al(110) surface displays normal inward relaxation, while Al(100) surface shows the ‘anomalous’ outward relaxation. To gain better understanding of the physical mechanism behind the ‘outward’ or ‘inward’ relaxations for

Table 4
Calculated forces on atomic layers in the unrelaxed geometry^a

Layer	Force (mRy au ⁻¹)	
	(100) unrelaxed	(110) unrelaxed
1	6.518	–6.943
2	5.986	10.767

^a Positive value indicates direction of force is towards the surface. Negative value indicates force is directed into the bulk.

Al(100) and Al(110), respectively, we have calculated the interplanar forces for the unrelaxed and relaxed geometries. The results are listed in Table 4. One can find that the force on the topmost layer of Al(100) is positive (toward surface) and drives the expansion, while that of Al(110) is negative (toward bulk) and drives the contraction.

An analysis of the electron density at the Al surface will help us to explain the behaviour of expansion and contraction. The respective charge densities of the Al(100) and Al(110) slabs have been plotted along the z axis (from bulk to vacuum) in Fig. 2. For Al(110), the electron density at the region between the first and second atomic layers increases after relaxation as indicated by the arrow in Fig. 2b, while for Al(100) the electron density decreases as indicated by the arrow in Fig. 2a,. This suggests an increased ‘back-bonding’ of the topmost layer to the second layer occurs in Al(110) while the reverse seems to take place in Al(100) resulting in the expansion. This decrease of the charge density in between the top two Al layers coupled by the increase of the charge density in the vacuum region near the surface is possibly the origin of the outward relaxation of the Al(100) surface.

5. Conclusion

In conclusion, we have used an ab initio pseudopotential method to study the multilayer relaxation of Al(100) and Al(110). Our calculations show that the surface relaxation of Al(100) is an ‘anomalous’ outward relaxation, while that of Al(110) is an inward relaxation, which are in excellent agreement with experimental results.

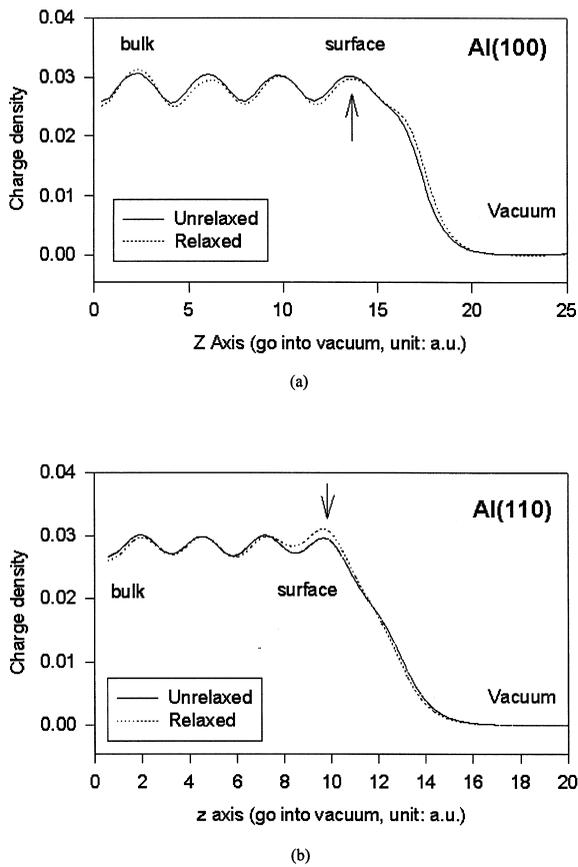


Fig. 2. Charge density of the Al(100) and Al(110) slabs along z axis (from bulk layers to the vacuum region).

Acknowledgements

The authors thank Dr S.-P. Li of Xiamen University (China) and Professor Y.P. Feng of National University of Singapore for helpful discussions.

References

- [1] J. Wan, Y.L. Fan, D.W. Gong, S.G. Shen, X.Q. Fan, *Model. Simul. Mater. Sci. Eng* 7 (1999) 189, and references therein.
- [2] D.L. Adams, V. Jensen, X.F. Sun, J.H. Vollesen, *Phys. Rev. B* 38 (1988) 7913.
- [3] N. Marzari, D. Vanderbilt, A. De Vita, M.C. Payne, *Phys. Rev. Lett.* 82 (1999) 3296.
- [4] H.L. Davis, J.B. Hannon, K.B. Ray, E.W. Plummer, *Phys. Rev. Lett.* 68 (1992) 2632.
- [5] P. Bohnen, K.M. Ho, *Surf. Sci.* 207 (1988) 105.
- [6] F. Jona, D. Sondericker, P.M. Marcus, *J. Phys. C: Solid State Phys.* 13 (1980) L155.
- [7] G.E. Laramore, C.B. Duke, *Phys. Rev. B* 5 (1972) 267.
- [8] D. Gebreselasie, G.A. Benesh, *J. Phys.: Condens. Mater* 9 (1997) 8359.
- [9] K.W. Jacobsen, P.M. Markus, F. Jona, *Phys. Rev. B* 6 (1972) 3684.
- [10] G.A. Benesh, D. Gebreselasie, *Phys. Rev. B* 54 (1996) 5940.
- [11] J.R. Noonan, H.L. Davis, *Phys. Rev. B* 29 (1984) 4349.
- [12] J.N. Andersen, H.B. Nielsen, L. Petersen, D.L. Adams, *J. Phys. C: Solid State Phys.* 17 (1984) 173.
- [13] H.B. Nielsen, J.N. Andersen, L. Petersen, D.L. Adams, *J. Phys. C: Solid State Phys.* 15 (1982) L1113.
- [14] H. Gobel, P. von Blanckenhagen, *Phys. Rev. B* 32 (1985) 3446.
- [15] K.M. Ho, K.P. Bohnen, *Phys. Rev. B* 32 (1985) 3446.
- [16] T. Ning, Q.L. Yu, Y.Y. Ye, *Surf. Sci.* 206 (1988) L857.
- [17] A.M. Rodriguez, G. Bozzolo, J. Ferrante, *Surf. Sci.* 289 (1993) 100.
- [18] R.N. Barnett, U. Landman, C.L. Cleveland, *Phys. Rev. B* 27 (1983) 6534.
- [19] S.P. Chen, D.J. Srolovitz, A.F. Voter, *J. Mater. Res.* 4 (1989) 62.
- [20] H.B. Nielsen, D.L. Adams, *J. Phys. C: Solid State Phys.* 15 (1982) 615.
- [21] J.R. Noonan, H.L. Davis, *J. Vac. Sci. Technol. A* 8 (1990) 2671.
- [22] D.L. Adams, H.B. Nielsen, M.A. Van Hove, *Phys. Rev. B* 20 (1979) 4789.
- [23] J.F. Van der Veen, R.C. Smeenk, R.M. Tromp, F.W. Saris, *Surf. Sci.* 79 (1979) 219.
- [24] I. Bartos, A. Barbievi, R.A. Van Hove, W.F. Chung, Q. Cai, M.S. Altman, *Surf. Rev. Lett.* 2 (1995) 477.
- [25] L. Hedin, B.I. Lundqvist, *J. Phys. C* 4 (1971) 2064.
- [26] D.R. Hamann, M. Schluter, C. Chiang, *Phys. Rev. Lett.* 43 (1979) 1494.
- [27] G.N. Kamm, G.A. Albers, *J. Appl. Phys.* 35 (1964) 327.
- [28] M. Bockstedte, A. Kley, J. Neugebauer, M. Scheffler, *Comp. Phys. Commun.* 107 (1997) 187.
- [29] P.J. Feibelman, *Phys. Rev. B* 46 (1992) 2532.
- [30] J.K. Norskov, N.D. Lang, *Phys. Rev. B* 21 (1980) 2131.
- [31] M.J. Stott, E. Zaremba, *Solid State Commun.* 32 (1979) 1297.
- [32] M.J. Stott, E. Zaremba, *Phys. Rev. B* 22 (1980) 1564.
- [33] M.S. Daw, M.I. Baskes, *Phys. Rev. B* 29 (1984) 6443.
- [34] W.R. Tyson, W.A. Miller, *Surf. Sci.* 62 (1977) 267.
- [35] J.P. Hirth, J. Lothe, *Theory of Dislocations*, McGraw-Hill, New York, 1968.